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A.M. Hodge[†], J. Biener, L.M Hsiung, A.V. Hamza, J.H. Satcher Jr.

Nanoscale Synthesis and Characterization Laboratory
Materials Science and Technology Division
Lawrence Livermore National Laboratory, CA 94550

Abstract

We describe a two-step dealloying/compaction process to produce nanocrystalline Au. First, nanocrystalline/nanoporous Au foam is synthesized by electrochemically-driven dealloying. The resulting Au foams exhibit porosities of 60 and 70% with pore sizes of ~ 40 and 100 nm, respectively, and a typical grain size of <50 nm. Second, the nanoporous foams are fully compacted to produce nanocrystalline monolithic Au. The compacted Au was characterized by TEM and X-ray diffraction and tested by depth-sensing nanoindentation. The compacted nanocrystalline Au exhibits an average grain size of <50 nm and hardness values ranging from 1.4 to 2.0 GPa, which are up to 4.5 times higher than the hardness values obtained from polycrystalline Au.

[†]Author to whom correspondence should be send
hodge4@llnl.gov

The superior mechanical properties of nanocrystalline (nc) materials, such as high yield strength and high wear resistance, have made their study an interesting subject [1, 2]. With some exceptions, processing of nc materials with grain sizes <100 nm has mostly been focused on elements such as Ni and Cu [2-5]. Finding new routes to produce nc materials can offer many advantages, such as producing materials which are not readily available, e.g. Au, and producing multiple grain sizes and larger specimens which are necessary factors to allow for comprehensive structural and mechanical tests. Synthesis of nc gold has undergone limited research, mostly consisting of gas deposition methods [6, 7] and some magnetron sputtering [8] with few studies on the mechanical behavior [9].

In this work, we demonstrate that by using a two-step dealloying/compaction process, one can obtain fully compacted, nc, monolithic gold with various grain sizes and superior mechanical behavior. The nc nanoporous Au is prepared by electrochemically-driven dealloying of Au/Ag alloys, and subsequently compressed to produce monolithic nc Au samples. Selective dealloying is a method by which the more electrochemically active element (Ag) is dissolved, leaving behind a sponge-like morphology of interconnecting ligaments made from the less electrochemically active element (Au) [10, 11]. Here we report the preparation of nc Au by a dealloying/densification method. In general, this procedure could be extended to prepare other nc materials.

Polycrystalline $Au_{0.3}Ag_{0.7}$ and $Au_{0.4}Ag_{0.6}$ alloy ingots were prepared by arc-melting Au (99.999%) and Ag (99.999%). The alloy composition was confirmed by a fire assay technique. Further foam processing details are discussed elsewhere [11, 12].

Only trace amounts of Ag were detected by energy dispersive X-ray (EDX) spectra after dealloying. Two different sample porosities were produced; 60 and 70%. The 70% porous sample had an average pore size of 100 nm, while the 60% porous samples had smaller pores on the order of 40 nm. Both porous samples were checked for grain size by using TEM and X-ray diffraction by applying Scherrer formula for peak broadening to the (111) reflections.

The porous samples were then placed in an Instron 4400R universal testing machine (Instron Corporation, Canton, MA) and compressed at room temperature. The compaction process continued until a fully compressed sample was obtained. A typical foam sample thickness was around 500 μm which was compressed to approximately 100 μm. Compressed samples were then tested by X-ray diffraction to identify the grain size and finally indented using both a Triboindenter (Hysitron, Inc., Minneapolis, MN) with a Berkovich tip and a standard Vickers microindenter to check hardness values.

The development of a nc grain structure was observed during dealloying and maintained during the compaction process described earlier. Figure 1 compares two SEM micrographs obtained from a) the original nanoporous structure, and b) an unpolished, fully compressed sample. Note that in the compressed sample there are some random voids but most of the sample presents a smooth-wavy surface. Additionally, more studies are currently underway to further improve the compression of the porous material, and the results will be presented in a future article.

The as prepared nanoporous sample as well as the compressed nc Au sample were characterized by X-ray diffraction and TEM. Both methods reveal that the as prepared nanoporous foam as well as the fully compressed Au sample, have grain sizes less than

50 nm, with the 60% porous Au showing an overall slightly smaller grain size. Figure 2 presents a TEM micrograph from a typical ligament for a 70% porous Au; indeed, multiple grain boundaries are observed per ligament. Furthermore, the acquired selective area diffraction (SAD) pattern, shown in Figure 2 is typical for a polycrystalline material, thus further proving that the individual ligaments are nanocrystalline. Table 1 compares the grain size dimensions obtained from the compressed nc Au which was processed from the 60 and 70% nanoporous gold samples as well as the grain size for polycrystalline gold (used for arc melting the original Au/Ag alloys).

The development of a nc grain structure is an unexpected result. In general, it is assumed that the dealloying process does *not* change the grain structure [10, 11, 13]. Nanoporous Au samples (100 nm thick) currently synthesized by other researchers [14] are made of single crystal ligaments in contrast to the nanoporous, nanocrystalline Au foams presented here and in our previous paper [12]. To our knowledge this is the first observation of recrystallization during dealloying towards a nanocrystalline grain structure.

We can only speculate why other researchers did not observe the evolving nanocrystallinity of the Au ligaments during dealloying which allows for the production of a compressed monolithic nc Au sample. However, a recent model proposed by Erlebacher et al.[10], suggests that dealloying of a Ag-Au alloy involves a dynamic rearrangement of the Au atoms, which could explain the evolution of the nc microstructure of nanoporous Au observed in the present study: selective dissolution of Ag atoms generates a supersaturation of Au adatoms and vacancies, which in turn results in the nucleation of Au adatom clusters and vacancy islands. The actual morphology

evolving under these conditions strongly depends on the mobility of vacancies and adatoms, and in particular of the presence of *nucleation sites*.

Table 1. Grain size and hardness values for compressed 60% and 70% porous Au foams

	Grain size		Hardness	
	X-ray (nm)	TEM (nm)	Triboindenter (GPa)	Vickers (GPa)
70% porous	21 (32-33)	(10-50)	1.44 ± 0.63	1.60 ± 0.24
60% porous	36.3 (34)	(10-50)	1.97 ± 0.48	1.26 ± 0.04
Polycrystalline Au (99.99%)	By optical microscopy ~140 μm		0.44 ± 0.04	0.45 ± 0.03

() denotes before compression

We have so far shown, by the use of TEM and X-ray diffraction, that our porous and compressed samples are indeed nanocrystalline. To further verify the nc nature of the compressed samples, indentation studies are presented in Table 1; the nc Au exhibit hardness values as high as 2.0 GPa. As a reference, we tested a polycrystalline Au sample by nanoindentation and Vickers microhardness; both tests resulted in nearly identical values around 0.45 GPa, which are accepted values for polycrystalline Au [15]. It has been demonstrated in other nc materials that in the range of grain sizes from 10 to 50 nm, the Hall-Petch relationship dictates that, as the grain size decreases, the hardness values should increase [2, 4]. Previous papers have presented nanoindentation experiments of Au, but not on nc Au [16, 17]. However, a direct comparison can be made with Sakai et al. [9], where nc Au specimens with 20-60 nm grain size were prepared by gas deposition method and showed hardness values in the range 0.8 to 2.0

GPa by Vickers microhardness; grain sizes <25 nm show hardness values above 1.0 GPa, which are in good agreement with our findings. It should be noted that nanoindentation could produce slightly higher hardness values than microhardness tests due to an artifact of surface work hardening from polishing and/or due to "indentation size effects". Our compressed sample was not polished, as can be seen in Figure 1b, so there should be no work hardening due to polishing. Using Vickers indentation allowed us to compensate for indentation size effects. Tests on the compressed samples by Vickers indentation yielded slightly lower values than those acquired by the Triboindenter, but the values were still up to 3.5 times higher than the polycrystalline sample, thus showing that there is a true increase in hardness values, consistent with the nanocrystalline character of our compressed Au samples.

In summary, we have presented a method to produce monolithic nc Au via a two-step dealloying/compaction process. The monolithic nc Au presented here has a grain size < 50 nm and exhibits an increased hardness over polycrystalline Au by a factor of 4.5. Further studies to improve the compaction process, are underway.

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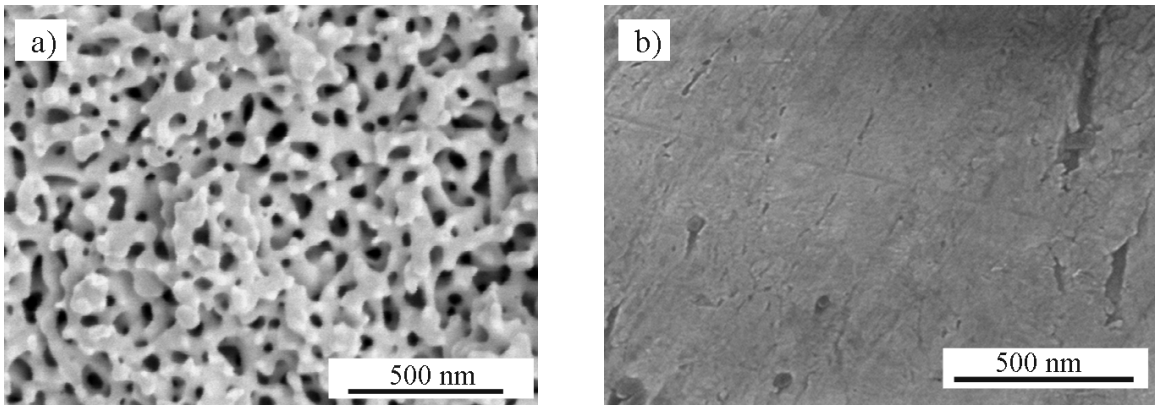

Figure 1 SEM micrographs obtained from a) syhthesized Au porous samples b) compressed Au sample

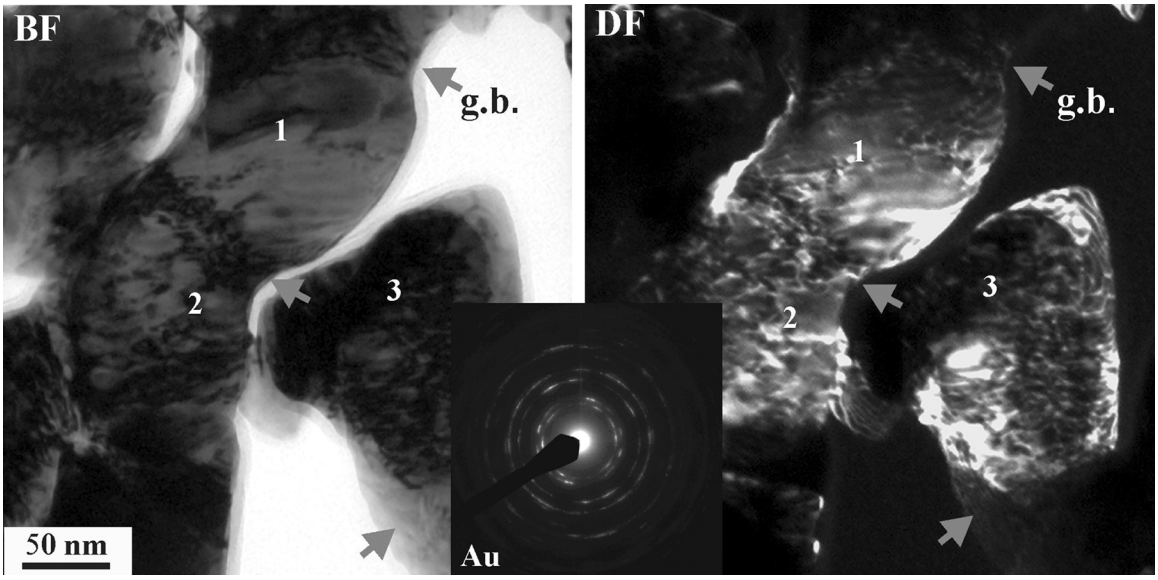

Figure 2. Dark field and bright field TEM micrographs of 70% porous sample showing three distinct grains <50 nm. Corresponding SAD pattern shown in inset.